the air-oxidation of Cu metal to Cu^{2+} ion.

Short Cu–Cu distances have been found in many di- or polynuclear Cu(I) complexes. However, all of these complexes have bridging ligands between copper atoms.[15,16] Moreover, MO calculations have not acknowledged the existence of direct Cu(I)–Cu(I) bonding of any significance.[15-17] The peak at 975 nm, therefore, may be due to charge-transfer between S1′ and Cu and not to the excitation of the electron in the Cu–Cu bonding orbital. More detailed studies are required to explain the nature of this peak.

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Supplementary Material Available: X-ray crystallographic data, results of cyclic voltammetry and magnetic measurements, and listings of bond angles and bond lengths for **2′** (8 pages). Ordering information is given on any current masthead page.

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(15) Cotton, F. A.; Wilkinson, G. *Advanced Inorganic Chemistry*, 4th ed.; John Wiley & Sons: New York, 1980; p 800.

(16) Clusters with Cu_8S_{12} core in which the copper atoms are bridged by sulfur atoms have also been reported: Hollander, F. J.; Coucouvanis, D. *J. Am. Chem. Soc.* **1977**, *99*, 6268–6280.

(17) For example: Mehrotra, P.; Hoffmann, R. *Inorg. Chem.* **1978**, *17*, 2187–2189.

A New Class of Homoleptic 12-Electron Molybdenum and Tungsten Alkoxide Clusters of Formula $[M_4(OR)_{12}]$

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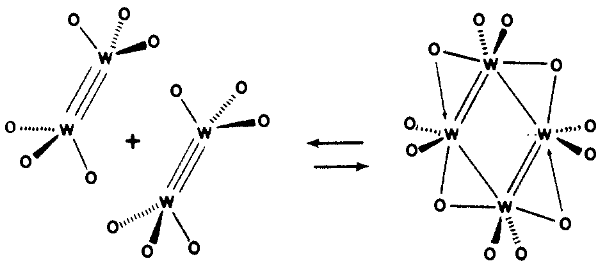
We are interested in developing efficient synthetic routes to alkoxide-supported molybdenum and tungsten clusters that may prove to be excellent models for fragments of reduced oxides of the same metals.[1] These clusters should include both coordinative unsaturation and redox flexibility at the metal centers to initiate organometallic chemistry upon substrate reduction. Complementary metal oxide model systems such as polyoxoanions may prove effective for oxidation catalysis.[2]

We have recently demonstrated that $W_2(O\text{-}i\text{-}Pr)_6$ (I) exists in reversible equilibrium with its 12-electron cluster $W_4(O\text{-}i\text{-}Pr)_{12}$ (II) in solution at room temperature, eq 1,[3] whereas $Mo_2(O\text{-}i\text{-}Pr)_6$ is indefinitely stable with respect to cluster formation.[4]



(1)

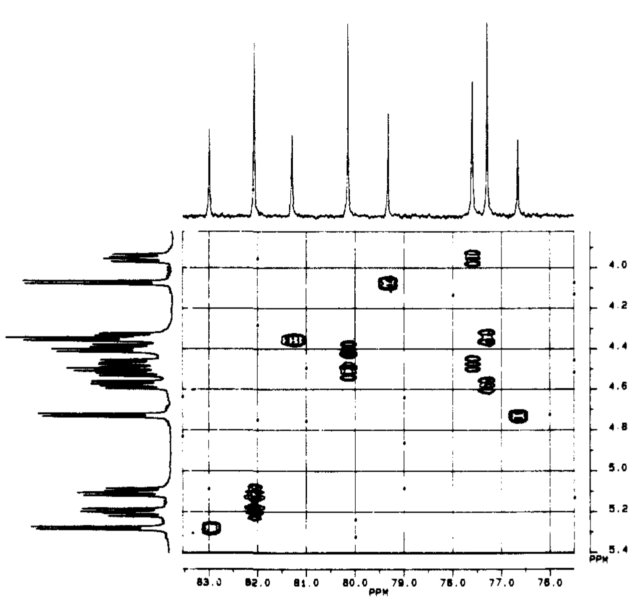


Figure 1. The ^{13}C–^{1}H 2D heteronuclear chemical shift correlated contour plot of the methylene region of XI showing the eight types of alkoxide ligands in the ratio 1:1:1:1:2:2:2:2. The carbon resonances of relative intensity 2 have inequivalent methylene protons. Spectrometer frequency = 500.13 MHz (^{1}H); 2D matrix: [1K (84 scans) × 256].

Even by reducing the steric demands at the molybdenum center we were unable to induce the formation of new metal–metal bonds in $[Mo_2(O\text{-}i\text{-}Pr)_5(OMe)]_2$ (III), which instead retains isolated, unbridged Mo–Mo triple bonds.[5] We report here the isolation and characterization of members of a new class of 12-electron tetranuclear alkoxide clusters, IV–XI, which are spectroscopically isostructural for both molybdenum *and* tungsten together with the single-crystal X-ray diffraction structure of one derivative, $[Mo_4(O\text{-}CH_2\text{-c-}Bu)_{12}(HO\text{-}CH_2\text{-c-}Bu)]$ (XI) (where c-Bu = cyclobutyl). This represents the first group of structurally related homoleptic alkoxide clusters for molybdenum and tungsten in oxidation state (3+).

Treatment of hexane solutions of $M_2(O\text{-}t\text{-}Bu)_6$ where M = Mo or W with >6 equiv of any of the alcohols, $HOCH_2R$, where R = cyclohexyl (Cy), isopropyl (*i*-Pr), cyclopentyl (Cp), or cyclobutyl (c-Bu), at room temperature results in immediate darkening of the solution to a deep green color. After having been stirred for 4 h, the volatile components are removed in vacuo, and by dissolving the residue in the minimum amount of 1,2-dimethoxyethane the following products crystallized upon cooling (−20 °C): $W_4(OCH_2\text{-}Cy)_{12}$ (IV), $W_4(OCH_2\text{-}i\text{-}Pr)_{12}$ (V), $W_4(OCH_2\text{-}Cp)_{12}$ (VI), $W_4(OCH_2\text{-c-}Bu)_{12}$ (VII), $Mo_4(OCH_2\text{-}Cy)_{12}$ (VIII), $Mo_4(OCH_2\text{-}i\text{-}Pr)_{12}$ (IX), $Mo_4(OCH_2\text{-}Cp)_{12}$ (X), and $Mo_4(OCH_2\text{-}Bu)_{12}$ (XI), respectively.[6]

The ^{1}H and ^{13}C NMR spectra of all these complexes, IV–XI, are consistent with a common, stereochemically *rigid* structural $[M_4O_{12}]_n$ unit in solution. In the ^{1}H NMR spectrum there is evidence for eight types of alkoxide ligands from the methylene proton resonances which are in the relative ratios 1:1:1:1:2:2:2:2. The resonances of relative intensity 2 arise from diastereotopic methylene protons, while those of intensity 1 are nondiastereotopic and can be distinguished at a spectrometer frequency of 500 MHz. A ^{13}C–^{1}H 2D heteronuclear chemical shift correlated contour plot (see Figure 1) clearly demonstrates the eight different types of alkoxide ligands as well as the relationship between the proton and carbon resonances. Thus the molecule contains a mirror plane of symmetry and is of lower symmetry than was observed for $W_4(O\text{-}i\text{-}Pr)_{12}$ (II). The elemental analyses are consistent with the empirical formula $[W(OR)_3]_n$, and the spectroscopic data dictate that the value of n is a multiple of four, e.g., $W_4(OR)_{12}$, $W_8(OR)_{24}$, ..., etc.[7] To establish the detailed nature of this new

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(1) Chisholm, M. H.; Folting, K.; Eichhorn, B. W.; Huffman, J. C. *J. Am. Chem. Soc.* **1987**, *109*, 3146 and references therein.

(2) Pope, M. T. In *Heteropoly and Isopoly Oxometallates*; Springer: New York, 1983. Day, V. W.; Klemperer, W. G.; Schwartz, C.; Wang, R. C. NATO Workshop Report, in press. Faraj, M.; Hill, C. L. *J. Chem. Soc., Chem. Commun.* **1987**, 1487.

(3) Chisholm, M. H.; Clark, D. L.; Folting, K.; Huffman, J. C. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 1014. Chisholm, M. H.; Clark, D. L.; Folting, K.; Hampden-Smith, M. J.; Huffman, J. C. *J. Am. Chem. Soc.* **1987**, *109*, 775; Chisholm, M. H.; et al. *J. Am. Chem. Soc.* submitted for publication.

(4) Chisholm, M. H.; Cotton, F. A.; Murillo, C. A.; Reichert, W. W. *Inorg. Chem.* **1977**, *16*, 1801.

(5) Chisholm, M. H.; Hammond, C. E.; Hampden-Smith, M. J.; Huffman, J. C.; Van Der Sluys, W. G. *Angew. Chem., Int. Ed. Engl.* 1987, *26*, 904.

(6) Satisfactory elemental analyses have been obtained.

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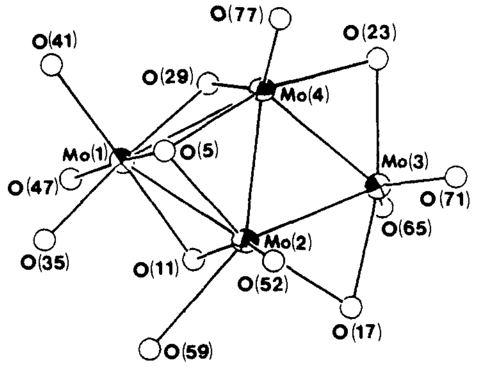

Figure 2. Ball-and-stick drawing of the central core of $Mo_4(OCH_2$-c-$Bu)_{12}(HOCH_2$-c-Bu). The metal–metal distances are as follows (Å): Mo(1)–Mo(2) = 2.66 (1), Mo(1)–Mo(4) = 2.68 (1), Mo(2)–Mo(4) = 2.46 (1), Mo(3)–Mo(4) = 2.47 (1), Mo(2)–Mo(3) = 2.51 (1). The esd's are averaged for the two independent molecules in the unit cell.

cluster type we attempted single-crystal X-ray diffraction studies on IV, V, VIII, IX, X, and XI. Unfortunately, the crystals obtained only diffracted to small angles, and it was concluded that the structure consisted of hexagonal close-packed molecules with a molecular disorder. However, a suitable crystal of a derivative of XI was obtained with lower symmetry, and the single-crystal X-ray diffraction structure was solved.[8]

The structure obtained for this species is shown in Figure 2 which satisfies the molecular formula $[M_4(OR)_{12}(HOR)]$ where an extra molecule of alcohol is present and has destroyed the symmetry and packing of the $M_4(OR)_{12}$ compound. The structure consists of a butterfly arrangement of metal atoms with one triangular face capped with a triply bridging alkoxide ligand, and each edge is bridged by alkoxide ligands. Mo(2) possesses one terminal alkoxide ligand and is also coordinated to another oxygen atom at a distance of 2.33 Å, in the range we have previously observed for metal-to-alcohol oxygen distances.[9]

The preference for this structure over that of II is probably a result of the smaller steric requirement of the alkoxide ligands O-CH_2R versus OR (same R) with the achievement of a greater number of M–O bonds and an octahedral coordination environment for Mo(1) providing a thermodynamic driving force.

Removal of the coordinated alcohol molecule from $Mo_4(OCH_2$-c-$Bu)_{12}(HOCH_2$-c-Bu) would allow the structure of XI to be consistent with the NMR spectroscopic data obtained for the remaining members of this cluster class. In solution it is possible that the alkoxide ligands denoted by O(41), O(5), O(65), and O(71) lie on a mirror plane which also passes through molybdenum atoms (1) and (3). This leaves eight alkoxide ligands related in a pair-wise manner by the mirror plane, accounting for the observed integral ratios. In benzene-d_6 solution crystals of $Mo_4(OCH_2$-c-$Bu)_{12}(HOCH_2$-c-Bu) dissociate the coordinated alcohol molecule, and XI exhibits similar NMR spectra to other members of this class.

The geometry of this new class of $M_4(OR)_{12}$ cluster is without precedent and taken together with the previous structures observed for $W_4(O$-i-$Pr)_{12}$[3] and $Mo_4X_4(O$-i-$Pr)_8$,[10] where X = Cl and Br, attests to the flexibility of metal–metal bonding in response to steric and electronic demands of the ancillary ligands.[11] Finally we note that this new class of $M_4(OR)_{12}$ compounds do *not* reversibly dissociate to form $M_2(OR)_6$ compounds, and coordinative unsaturation is maintained at three of the four metal sites. These are potentially available for substrate activation.[12]

Supplementary Material Available: A listing of fractional coordinates and bond distances and bond angles for the central Mo_4O_{13} moiety and stereoview of the molecules (9 pages). Ordering information is given on any current masthead page.

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(7) A cryoscopic molecular weight determination on the compound $[Mo_4(OCH_2$-i-$Pr)_{12}]_n$ indicated that $n = 1$.

(8) Crystal data for $Mo_4(OCH_2$-c-$C_4H_8)_{12}(HOCH_2$-c-$C_4H_8)$ at −156 °C: $a = b = 19.952$ (7) Å, $c = 34.755$ (16) Å, $d_{calcd} = 1.432$ g cm^{-3}, $Z = 8$ and space group $P4_1$ (no. 76). Of 11 293 reflections collected, Mo Kα, $6° < 2\theta < 45°$, 9263 were unique, and the 7977 reflections having $F > 3.0\sigma(F)$ were used in the least-squares refinement. $R(F) = 0.058$ and $Rw(F) = 0.058$.

(9) Chisholm, M. H. *Polyhedron* **1983**, *2*, 681.

(10) Chisholm, M. H.; Errington, R. J.; Folting, K.; Huffman, J. C. *J. Am. Chem. Soc.* **1982**, *104*, 2025.

(11) Chloromolybdate ions, $Mo_4Cl_{12}^{3-}$, having 15 electrons available for M–M bonding have been found to adopt one of either rectangular or butterfly Mo_4 geometries in the solid state depending upon the nature of the counter cation: Aufdembrink, B. A.; McCarley, R. E. *J. Am. Chem. Soc.* **1986**, *108*, 2474.

(12) We thank the Department of Energy, Office of Basic Sciences, Chemistry Division for support of this work.

Synthesis of Bicyclic Keto Silanes by Tandem Rearrangement of Silylacetylenic Ketones

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In developing a general route to differentially functionalized fused bicyclic systems we have explored the thermal rearrangement of cycloalkanones bearing an ω-silylacetylenic chain β to the carbonyl group. We now report that the prototype system **1a** undergoes a novel sequence of tandem rearrangements leading to the bicyclic dienol silane **2a** and that by appropriate structural modifications we can alter the reaction pathway to provide a new, high-yield synthesis of bicyclic allylsilane ketones.

When ketone **1a**[1] was held at 300 °C (neat, 2 h), the major product (60–65% yield) was a carbonyl-free isomer[2] showing by 300 MHz ^1H NMR an allylic CH_3 (3 H, δ 1.96, s), an olefinic proton at δ 4.93 (1 H, m), and $OSiMe_3$ at δ 0.22 (9 H, s). Since this product could be quantitatively hydrolyzed in wet tetrahydrofuran to the known conjugated ketone **3a**[3] and dehydrosilylated ($Pd(OAc)_2$, MeCN, room temperature, 14 h, 59% yield)[4] to the cross-conjugated dienone **4a**,[5] its structure was established as the dienol silane **2a**.[2]

The unexpected formation of dienol silane **2a** from acetylene **1a** could be rationalized by a multiple rearrangement sequence proceeding through initial enolization of **1a** to **5a**, Conia cyclization[6,7] to vinylsilane **6a**, prototropic double bond migration to conjugated enone **7**, followed by Casey rearrangement[8] of silicon to oxygen giving **8**, and a final prototropic rearrangement to the more stable diene tautomer **2a** (Scheme I).

If the indicated mechanism is correct, placement of an alkyl group at C-2 in **1**, leading to **6b**, would prevent isomerization to **7** and arrest the reaction at the vinylsilane stage. However, when

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(1) Ketones **1** were synthesized by conjugate addition of the appropriate ω-trimethylsilylalkynylmagnesium chloride (THF, 0.45 equiv of CuI) to the corresponding conjugated enone, as described by House and Fischer (House, H. O.; Fischer, W. F. *J. Org. Chem.* **1969**, *34*, 3615). All ketones **1** were fully characterized by IR, NMR, combustion analysis, and MS and distilled before use. The α-methyl ketones **1b–e** were used as cis/trans mixtures. Ketone **1a**: IR (film) 2175, 1710 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 2.28 (3 H, m), 2.16 (2 H, t), 1.93 (4 H, m), 1.56 (1 H, m), 1.47 (2 H, dt), 1.27 (1 H, m), 0.04 (9 H, s); MS, 222 (M^+). Anal. Calcd for $C_{13}H_{22}OSi$: C, 70.21; H, 9.97. Found: C, 70.32; H, 9.99.

(2) Enolsilane **2a**: ^1H NMR (300 MHz, $CDCl_3$, partial) δ 4.89 (1 H, m), 1.96 (3 H, s), 0.22 (9 H, s); IR no C=O; MS, calcd for $C_{13}H_{22}OSi$ 222.1440, found 222.1405; UV (MeOH) λ_{max} 252 nm, ε 11 927.

(3) Weisbuch, F.; Yamagami, C.; Dona, G. *J. Org. Chem.* **1972**, *37*, 4334.

(4) Ito, Y.; Hirao, T.; Saegusa, T. *J. Org. Chem.* **1978**, *43*, 1011.

(5) Dienone **4a**: ^1H NMR (400 MHz, $CDCl_3$, partial) δ 6.70 (1 H, ddd, $J = 10, 7, 3$), 5.80 (1 H, dd, $J = 10, 3$), 2.10 (3 H, s).

(6) For a review, see: Conia, J. M.; LePerchec, P. *Synthesis* **1975**, 1.

(7) Thermal cyclizations of simple acetylenic ketones have been reported by Agosta and Wolff (Agosta, W. C.; Wolff, S. *J. Org. Chem.* **1975**, *40*, 1699) and by Drouin et al. (Drouin, J.; Leyendecker, F.; Conia, J. M. *Tetrahedron Lett.* **1975**, 4053). Mercuric ion-catalyzed cyclizations of ε-acetylenic ketones are known, cf.: Boaventura, M. A.; Drouin, J.; Conia, J. M. *Synthesis* **1983**, 801.

(8) Casey, C. P.; Jones, C. R.; Tukada, H. *J. Org. Chem.* **1981**, *46*, 2089.

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